Tetraalkylammonium Salt as Photoinitiator of Vinyl Polymerization in Organic and Aqueous Media: A Mechanistic and Laser Flash Photolysis Study

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ABSTRACT: *N*-Dimethyl-*N*-[2-(*N,N*-dimethylamino)ethyl]-*N*-(1-methylnaphthyl)ammonium tetrafluoroborate (**I**) was synthesized with the aim of obtaining a versatile photoinitiator for vinyl polymerization in organic solvents and water. Salt **I** was able to trigger the polymerization of acrylamide, 2-hydroxyethylmethacrylate and styrene even at very low concentrations of the salt ($\sim 1.0 \times 10^{-5}$ M). Using laser flash photolysis and fluorescence techniques and analyzing the photoproduct distribution, we were able to postulate a mechanism for the photodecomposition of the salt. With irradiation, **I** undergoes an intramolecular electron-transfer reaction to form a radical ion pair (RIP). The RIP intermediate decomposes into free radicals. The RIP and the free radicals are active species for initiating the polymerization. Depending on the concentration of the vinyl monomers studied, the initiation mechanism of the polymerization reaction changes. At large monomer concentrations, the RIP state is postulated to trigger the reaction by generating the anion radical of the olefin substrate. At a low monomer concentration, the free radicals produced by the decomposition of **I** are believed to start the chain reaction. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 901–913, 2002; DOI 10.1002/pola.10166

Keywords: photopolymerization; radical polymerization; initiators; charge transfer; tetraalkylammonium salt

INTRODUCTION

The synthesis of new photoinitiators for vinyl polymerization is a subject of current interest because of its widespread technological applications.[1–3] As a result, in addition to those photoinitiators already known, new systems able to start the polymerization of vinyl monomers are reported every year.

Even though the selection of the appropriate initiator strongly depends on the desired characteristics of the polymeric material, for most applications it is always desirable to obtain the polymer free of additives and/or starting monomer material, or both. Moreover, the possibility of avoiding the use of volatile organic solvents for carrying out the solvent-free (in-bulk) polymerizations or, at least, replacing them with water is an attractive idea because it offers tremendous environmental advantages.

Besides the solubility and thermostability requirements, the achievement of these goals imposes two main characteristics on the photoinitiator system: (1) it must exhibit a significant molar absorption coefficient to minimize its use as additive and (2) it should be able to photogenerate active species by a unimolecular process. The second requirement is essential if high degrees of monomer conversion are required. Unimolecular photogeneration of new centers of polymerization largely increases the possibility of reaching almost complete monomer consumption, avoiding

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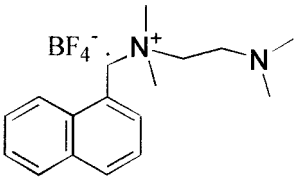
the problem of increasing viscosity of the medium as the polymerization reaction progresses. Therefore, the use of photoinitiator systems that require a chromophore and a coinitiator is discouraged for many applications and, evidently, is of no use in the polymerizations in bulk of most commercial monomers. However, the difficulties with diffusion could be alleviated if the coinitiator is covalently linked to the initiator or if it is contained either in the monomer or in a part of the structure of the polymer formed.

It is known that the polymerization of acrylamide (AA), 2-hydroxyethylmethacrylate (HEMA), styrene, and other vinyl monomers can be initiated by a variety of active free radicals. It is also known that these vinyl substrates are relatively good electron acceptors,[4,5] which allows the generation of the corresponding anion radicals either electrochemically or through a photoinduced or thermal electron-transfer (ET) reaction. It has been suggested that in aprotic solvents the anion radical is able to trigger the chain reaction.[5–7] In the presence of a proton source, the vinyl anion radical yields the corresponding neutral radical, which also acts as an active species. For instance, it is known that the electropolymerization of AA and HEMA in water is initiated by a neutral free radical, which is produced by a reaction of the monomer with the hydrogen radicals generated in the cathode from the reduction of the solvent.

In parallel, several photoinitiator systems believed to generate the anion radical of the vinyl monomer as an initiator of the polymerization have been reported. These systems employ polyaromatic hydrocarbon compounds[8–11] or transition-metal complexes[4,12–15] as chromophores and an aliphatic amine as a coinitiator. Note that in these photoinitiator systems, the active species are generated bimolecularly and therefore, relatively coinitiator large concentrations are generally required.

As mentioned previously, the diffusive problems can be palliated by the linking of the initiator to the coinitiator. To this effect, Neckers and Jager[3] studied the generation of free radicals after the photolysis of arylammonium tetraphenylborate salts, radicals that can be potential triggers of vinyl polymerization. In low-polarity media, these salts dissolve as contact ion pairs; this facilitates the ET reaction between the excited chromophore (the arylammonium cation) and borate ion. Because of the nature of these systems, the efficiency of these salts as photoinitiators should be diminished in polar solvents because diffusion of the ions is required for the ET reaction to take place.



I

Scheme 1

With these ideas in mind, we synthesized the salt *N*-dimethyl-*N*-[2-(*N*,*N*-dimethylamino)ethyl]-*N*-(1-methylnaphthyl)ammonium tetrafluoroborate (**I**) with the aim of obtaining a versatile photoinitiator capable of initiating vinyl polymerization in water and organic solvents (Scheme 1). It is known that compounds structurally related to **I** undergo a photoinduced intramolecular ET reaction upon excitation of the naphthalene chromophore.[16] In such a reaction, the aromatic hydrocarbon behaves as an electron acceptor (A), and the terminal amino group acts an electron donor (D). Reduction of the naphthalene moiety in **I** should produce the corresponding anion radical that, in principle, must be able to reduce the vinyl substrate, triggering the chain reaction. In this system, the amine group at the end of the alkyl chain acts as a coinitiator. However, because it is covalently linked to the aromatic group, **I** should unimolecularly photogenerate the active species. In fact, **I** proved to be an effective initiator of vinyl polymerization in all the media studied even when used at concentrations lower than 1.0×10^{-5} M. The ammonium group in **I** was included to increase its solubility in water.

In this article is reported a study on the mechanism of the photodecomposition of salt **I** and on the interactions of the photogenerated intermediate species with several vinyl monomers. The understanding of the mechanism by which the salt attains the initiation of chain reaction is important for proposing new photoinitiators.

EXPERIMENTAL

General

Absorption spectra were recorded with a Hewlett–Packard 8453 diode array ultraviolet–visible spectrophotometer. Stationary fluorescence quenching experiments were carried out with a Spex Fluoromax spectrofluorometer. Fluorescence lifetimes were determined by the time-correlated single-photon-counting technique with an Edinburgh In-

struments OB-900. ^{1}H NMR spectra were registered with a 200-MHz NMR instrument.

Steady-State Photolysis and Quantum Yields

Continuous photolysis experiments were performed with a monochromatic illumination system (Photon Technology International) equipped with a 150-W xenon lamp. The irradiation wavelength was set at 318 ± 5 nm. All experiments were carried out at 25 ± 0.5 °C. The actinometer used was an Aberchrome 540 from Aberchromics, Ltd., in toluene. The actinometer sample was irradiated at 1-min intervals for 30 min, and the depletion of the absorption at 343 nm was recorded as a function of time. The intensity of the incident light was calculated with the reported value of 0.20 for the quantum yield of the actinometer in the 310–370-nm excitation range.[17] Under the same conditions, deaerated solutions of **I** were irradiated. The conversion of the starting material was always kept below 2%.

The chromatographic identification and quantification of photoproducts were performed with a Hewlett–Packard 5890 chromatograph equipped with an HP-1 crosslinked methyl silicone gum column and an HP 5972 mass selective detector calibrated with commercial or synthesized standard compounds.

Flash Photolysis Experiments

Transient decays and absorption spectra were determined with a Spectron SL400 Nd:YAG laser generating 266 nm (~18-ns pulse width). The laser beam was defocused to cover the entire path length (10 mm) of the analyzing beam from a 150-W xenon lamp. The experiments were performed with rectangular quartz cells with right-angle geometry. The cell holder was thermostated by water circulation. The detection system consisted of a Photon Technology International monochromator coupled to a Hamamatsu R666 PM tube. The signal was acquired with a digitizing scope (Hewlett–Packard 54504); it was averaged and then transferred to a computer.

Deaerated samples of **I** were prepared to have an absorption of 0.40. All the experiments were carried out with fresh solutions with the continuous flow technique. K_2CrO_4 filters were used to vary the laser light intensity.

Photopolymerization Experiments

The polymerization experiments were carried out in a Rayonet model RPR-100 merry-go-round photochemical reactor supplied with two RPR-3000A lamps.

In a typical experiment, a 2.5-mL deaerated solution containing the monomers (1 M) and the photoinitiator (1.2×10^{-5} M) was irradiated to a given time. The polymer was precipitated from the photolyzed solution with a 50-fold volume excess of methanol, filtered, and gravimetrically evaluated. Reported results correspond to the average of at least two experiments. All experiments were carried out at 25 ± 0.5 °C.

Synthesis and Materials

2-Propanol, methanol, and toluene [all the solvents were Sintorgan high performance liquid chromatography (HPLC)-grade] were used as received. Dichloromethane and acetonitrile (Sintorgan) were dried with CaH_2 and stored over molecular sieves. The experiments in aqueous solutions were carried out at pH 11 by the addition of sodium hydroxide. AA, HEMA, and styrene were provided by Aldrich. AA was used as received. HEMA was vacuum-distilled before being used. Styrene was distilled, and the fraction in the 145–146 °C temperature range was employed. 1-Hydroxymethylnaphthalene (Aldrich) was used as received. Naphthalene (Aldrich) was sublimated before use.

1-(*N,N*-Dimethylamino)methylnaphthalene (AMN) was synthesized by the $LiAlH_4$ reduction of the corresponding amide, which was prepared from 1-naphthalene carboxylic acid and dimethylamine.

ELEM. ANAL. Calcd. for $C_{13}H_{15}N$: C, 84.3%; H, 8.2%; N, 7.6%. Found: C, 84.27%; H, 8.24%; N, 7.59%. ^{1}H NMR ($DCCl_3$): 7.3–8.1 (m, 7H), 3.75 (s, 2H), 2.8 (s, 6H). Mass: 58, 115, 127, 141, 168, 185.

I was synthesized from 1-chloromethylnapthalene and *N,N′*-tetramethylethylenediamine according to the procedure described by Arnold et al.[18] The initially obtained chloride salt was dissolved in water and precipitated as the tetrafluorate by the addition of a saturated solution of $NaBF_4$. The solid (salt **I**) was recrystallized from water and exhaustively dried at 50 ° C under a nitrogen atmosphere.

ELEM. ANAL. Calcd. for $C_{17}H_{25}N_2BF_4$: C, 59.1%; H, 7.3%; N, 8.1%. Found: C, 59.12%; H, 7.27%; N, 8.11%. ^{1}H NMR (DMSO-d_6): 7.6–8.3 (m, 7H), 5.04 (s, 2H), 4.05 (t, 2H), 3.06 (s, 6H), 2.14 (t, 2H), 1.93 (s, 6H).

The oxidation (E_{ox}) and reduction (E_{red}) potentials of **I** were measured in acetonitrile with the cyclic voltammetry technique. A Pt microelectrode was used as the working electrode, and

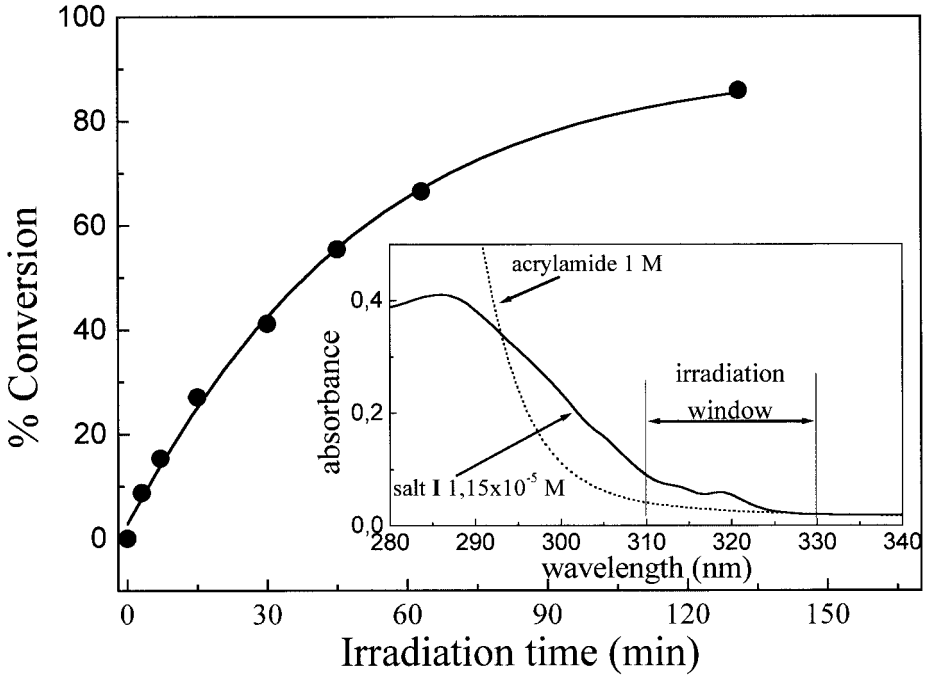


Figure 1. Conversion profile for AA in the presence of salt **I** as a function of the irradiation time. The insert shows the absorption spectra of AA (1 M; dotted line) and salt **I** (1.15×10^{-5} M; solid line) in water.

$NaBF_4$ (0.1 M) was used as the supporting electrolyte. The obtained cyclic voltagram showed two irreversible waves centered at approximately −2.03 and +0.98 V versus standard calomel electrodes (SCE). The cathodic process was assigned to the reduction of the aromatic nucleus of the salt. A similar E_{red} value was reported for the reduction of *N,N,N*-tributyl-*N*-(2-naphthylmethyl)ammonium tetraphenylborate under similar conditions.[19] The E_{ox} value of **I** is in agreement with that expected for the oxidation of a tertiary amine.

RESULTS AND DISCUSSION

Photopolymerization

The efficiency of **I** as the photoinitiator of the radical polymerization of AA and HEMA was studied in aqueous solutions at pH 11. In Figure 1, the profile of conversion for AA in the presence of **I** is shown as a function of the irradiation time. The insert in Figure 1 shows the absorption spectra of the salt and that of the monomer at the concentrations used in the photolysis experiments. An inspection of the figure shows that the conversion limit reached is larger than the 80%. The efficiency of **I** as the photoinitiator of the two monomers was also studied in acetonitrile, although the conversion limit in this cases did not exceed 60%. Good conversion yields were obtained for HEMA and styrene in dichloromethane. In-bulk polymerizations of HEMA and styrene were not carried out because both monomers showed an important absorption at 320 nm.

Characterization of the Photoinitiator

To explain these results, we studied the kinetics of the photodecomposition of **I**, putting particular emphasis on the characterization of the reaction intermediates able to initiate the polymerization of the vinyl substrates.

The absorption and fluorescence spectra of **I** recorded in dichloromethane, acetonitrile, and aqueous solutions were very similar to those observed for 1-methylnaphthalene (MN) in organic media. The salt is thermally stable in the solvent studied, even in water at basic pH. This is supported by the lack of detection of the expected hydrolysis product of the salt (1-hydroxymethylnaphthalene) by gas chromatography/mass spectrometry.

I presents a very weak fluorescence in dichloromethane, acetonitrile, or basic aqueous solutions. The emission in these media occurs around

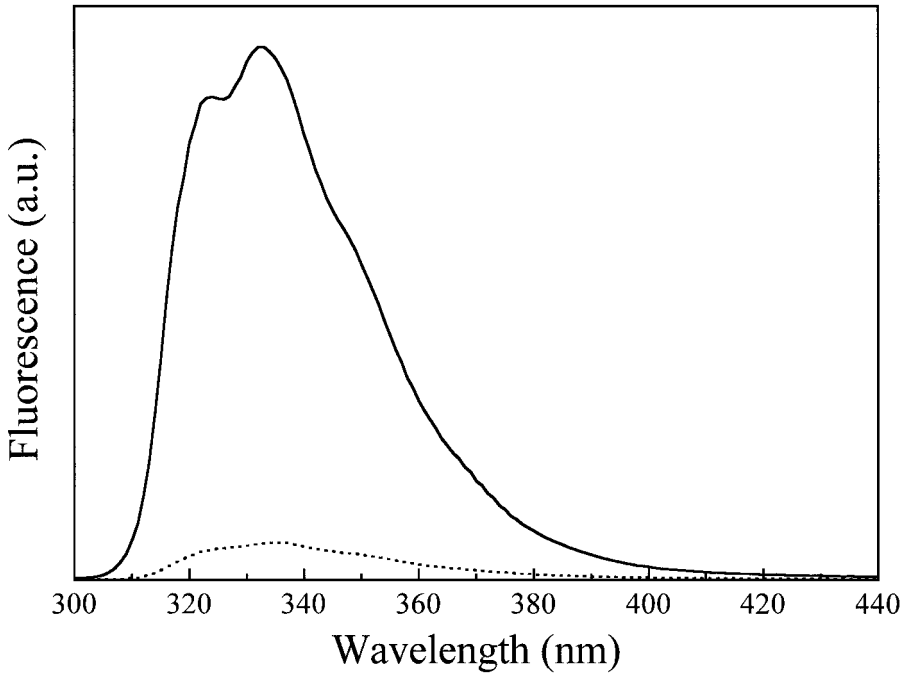


Figure 2. Fluorescence spectra of salt **I** at pH 4 (dotted line) and pH 11(solid line).

350 nm, and it is assigned to the aromatic chromophore. Other than that, no new fluorescence bands that could be attributed to the formation of an excited-state complex (or exciplex) were observed. The emission of the salt becomes relatively more important in acid or neutral aqueous media. Figure 2 shows the emission spectra of **I** at pHs 4 and 11. The emission of **I** decreases with increasing pH, and it is recovered by acidification of the solution. This suggests that the terminal amino group is involved in an acid–base equilibrium. Therefore, the poor emission of **I** (in basic pHs and aprotic media) can be ascribed to the intramolecular quenching of the aromatic chromophore by the terminal amino group. This assumption is supported by several experimental reports indicating that emission quenching of the singlet excited state of naphthalene by aliphatic amines is an efficient process, quenching that is known to occur through an ET mechanism.[16]

At pH 4, the emission of **I** decays monoexponentially with an associated fluorescence lifetime of approximately 3.4 ± 0.1 ns. This value is in agreement with that reported by Pincock et al.[20] for 1-naphthylmethyltrimethylammonium chloride in methanol (3.82 ns). Because of the low fluorescence quantum yield shown by **I** in basic aqueous solutions (and in aprotic media) and because it decomposes with irradiation, the determination of the emission decay time in these media is difficult. The emission decay of **I** (at pH 11) requires a biexponential fit with lifetimes of 0.3 ± 0.1 ns and 25.0 ± 0.1 ns. The very short emission decay time is compatible with that expected for the naphthalene chromophore being intramolecularly quenched by the free amino group. The second component probably corresponds to the decomposition product because its statistical weight increases quickly as the solution is photolyzed.

The fluorescence of **I** in a basic aqueous solution is not affected by the presence of 0.5 M AA (or HEMA). At the concentration of the monomers used for the polymerization experiments (1 M), a small reduction of the emission intensity of **I** is observed. In principle, this effect cannot be ascribed to a quenching process because the solvent composition in this case is significantly modified.

Photolysis of **I** at pH 11 yields MN and AMN. Both products were identified by a comparison of their mass spectra (and retention times) with those of standard compounds with a gas chromatograph/mass spectrometer. The quantum yields for the formation of MN (Φ_{MN}) and AMN (Φ_{AMN}) at pH 11 were measured. In Figure 3, a plot of the concentration of photoproducts formed upon photolysis is shown as a function of the irradiation time. From the slope of these plots and using Aberchrome 540 as an actinometer, values of 0.015 ± 0.005 and 0.008 ± 0.003 were calculated for Φ_{MN} and Φ_{AMN},

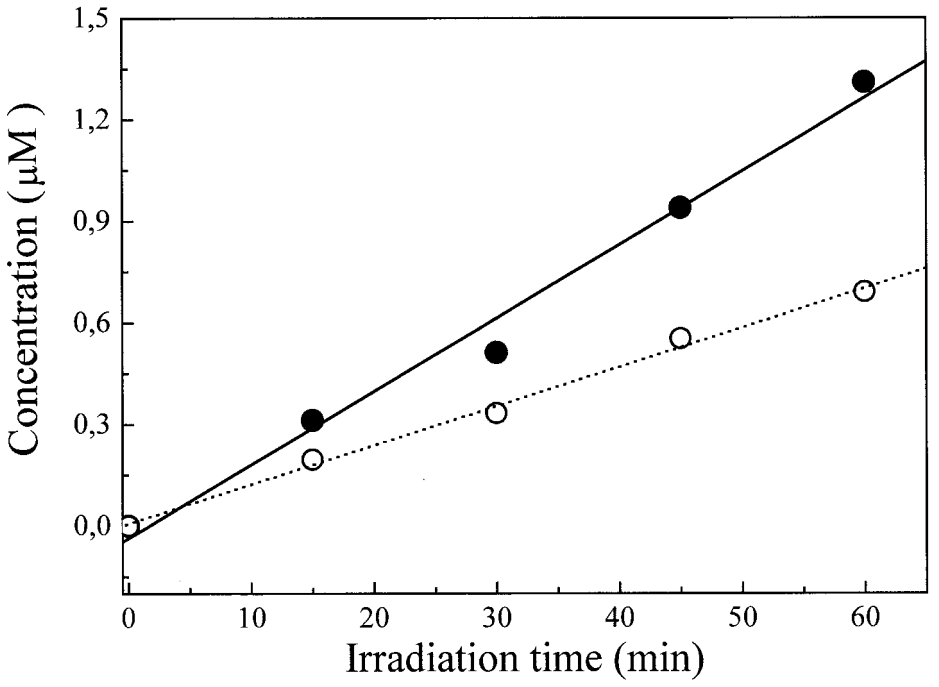


Figure 3. Dependence of the concentrations of (●) MN and (○) AMN as functions of the irradiation time during the photolysis of a deaerated aqueous solution of **I** (1.2×10^{-5} M).

respectively. A study of the photoproduct distribution in the presence of AA was not possible because the polymerization of the monomers made impracticable the chromatographic analysis of the samples. The photolysis of **I** in aprotic solvents such as acetonitrile or dichloromethane gave 1-methylnaphathalene and a series of products that could not be identified. No attempts to estimate the quantum yields of the photoproducts in these solvents were made.

Figure 4 shows the absorption spectra of transient species corresponding to **I** in aqueous basic solutions obtained by laser flash photolysis. The spectra were recorded 1 and 20 μs after the laser excitation pulse at 266 nm. The absorption (centered at ~420 nm) at 1 μs is assigned to the triplet excited state of the 1-methylnaphtalene chromophore,[21] whereas the remaining absorption at 20 μs (centered at ~330 nm) corresponds to the 1-naphthylmethyl free radical.[22] Similar results were obtained in acetonitrile.

The insert in Figure 4 shows the temporal evolution of both transient absorptions. The triplet state decay can be fitted monoexponentially with a lifetime (τ_0^T) of approximately 5 μs. On the other hand, the 1-naphthylmethyl free-radical absorption shows a fast initial rise followed by a second growth component that is in line with the triplet excited-state lifetime. Unfortunately, a detailed analysis of the signal profile for a short timescale (<500 ns) is not possible because of the inherent resolution of our instrumental setup. The temporal evolution of the transient absorptions does not change with the concentration of the salt (varied between 1.0×10^{-5} and 3.0×10^{-4} M) or with the addition of a 15-fold excess of $NaBF_4$. These results indicate that extrapolation at a zero concentration of the salt is not required for the calculation of the quantum yields of the transients.

Figure 5 shows a plot of the absorbance of the 1-naphthylmethyl free radical measured at 330 nm ($A_{330}^{R\cdot}$) as a function of the laser intensity. In the same figure is also shown the dependence on the laser intensity of the triplet–triplet absorption of naphthalene in cyclohexane measured at 413 nm. The naphthalene triplet–triplet absorption was used as an actinometer. With matched absorptions for both solutions at 266 nm, the quantum yield for the formation of the 1-naphthylmethyl free radical ($\Phi_{R\cdot}$) can be experimentally calculated according to the following:

$$\Phi_{R\cdot} = \left(\frac{\varepsilon_{413}^{N}}{\varepsilon_{330}^{R\cdot}}\right)\left(\frac{S_{330}^{R\cdot}}{S_{413}^{N}}\right)\Phi_{isc}^{N} \qquad (1)$$

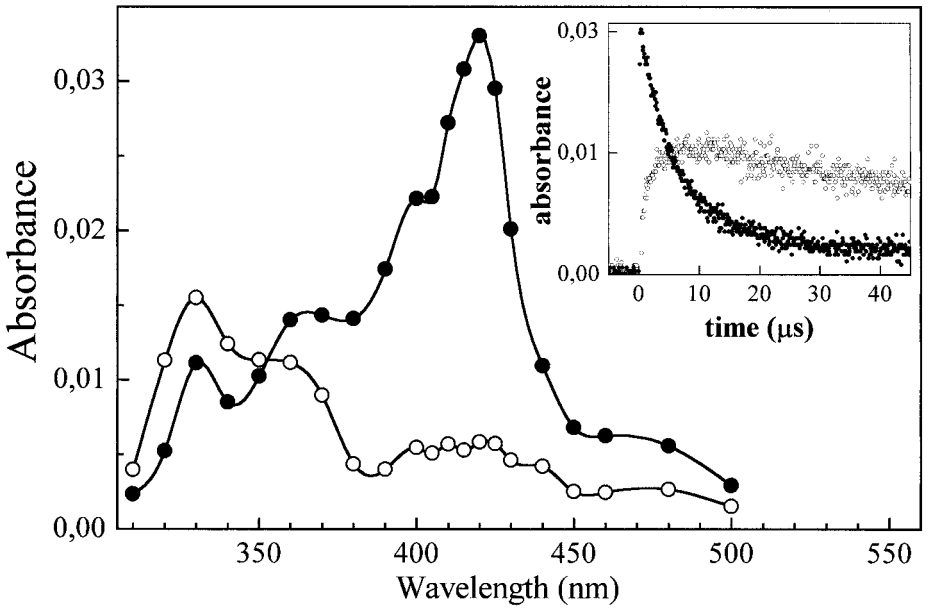


Figure 4. Absorption spectra of transient species corresponding to salt **I** in aqueous basic solutions. The spectra were recorded at (●) 1 and (○) 20 μs after the laser excitation pulse at 266 nm. The absorption centered at 420 nm at 1 μs is assigned to the triplet excited state of the MN chromophore, whereas the remaining absorption at 20 μs centered at 330 nm corresponds to the 1-naphthylmethyl free radical. The insert shows the temporal evolution of both transient absorptions: the triplet excited state of (●) MN and (○) the 1-naphthylmethyl free radical.

where $S^{R^\cdot}_{330}$ and S^{N}_{413} represent the initial slopes of the plots in Figure 5, $\epsilon^{R^\cdot}_{330}$ and ϵ^{N}_{413} (22,600 M^{-1} cm^{-1})[23] are the corresponding absorption coefficients, and Φ^{N}_{isc} (0.75)[24] stands for the quantum yield for intersystem crossing of naphthalene in cyclohexane. Unfortunately, the absorption coefficient for the 1-naphthylmethyl radical ($\epsilon^{R^\cdot}_{330}$) is not an easily accessible value; consequently, the absolute quantum yields for radical formation ($\Phi_{R^\cdot}$) cannot be determined without a large uncertainty. If $\epsilon^{R^\cdot}_{330}$ is taken to be the same as that reported for the 1-naphthylmethyl anion radical, that is, approximately 20,000 ± 10,000 M^{-1} cm^{-1},[25] an approximated value of $\Phi_{R^\cdot} = 0.06 \pm 0.04$ can be estimated. Note that this value of $\Phi_{R^\cdot}$ is larger than that measured for the quantum yield of MN ($\Phi_{MN} = 0.015 \pm 0.005$). Whether the observed difference between $\Phi_{R^\cdot}$ and Φ_{MN} indicates that part of the free radical disappears to give other products than MN or if it is just the consequence of an inappropriate value chosen for $\epsilon^{R^\cdot}_{330}$ in the calculation of $\Phi_{R^\cdot}$ cannot be unambiguously decided. The radical decays by pseudo-first-order kinetics with a lifetime of approximately 100 μs, which does not change with an increase of the concentration of **I** or BF_4^-. Consistently, the lack of detection (by gas chromatography/mass spectrometry) of 1,2-dinaphthylethane as a photoproduct indicates that the radical coupling reaction is not occurring. When the photolysis of **I** is carried out in alkaline deuterated water, the MN obtained shows the incorporation of a deuterium atom. This fact is apparent from the mass spectrum of the photoproduct, which shows prominent M and M + 1 picks at 143 and 144 au, respectively. In principle and on the basis of thermodynamic considerations, it can be shown that the 1-naphthylmethyl radical cannot abstract a hydrogen atom directly from water. Therefore, the hydrogen source for the formation of MN from the 1-naphthylmethyl free radical is still not clear.

In Figure 5 is also shown a plot of the triplet–triplet absorption of **I** measured at 420 nm as a function of the intensity of the incident light. From these experimental data, the quantum yield for the intersystem crossing of **I** at pH 11 (Φ^{I}_{isc}) can be estimated according to eq 2:

$$\Phi^{I}_{isc} = \left(\frac{\varepsilon^{N}_{413}}{\varepsilon^{MN(T)}_{420}}\right)\left(\frac{S^{I(T)}_{420}}{S^{N}_{413}}\right)\Phi^{N}_{isc} \qquad (2)$$

where $S^{I(T)}_{420}$ is the slope of the plot and $\epsilon^{MN(T)}_{420}$ represents the absorption coefficient for the triplet–

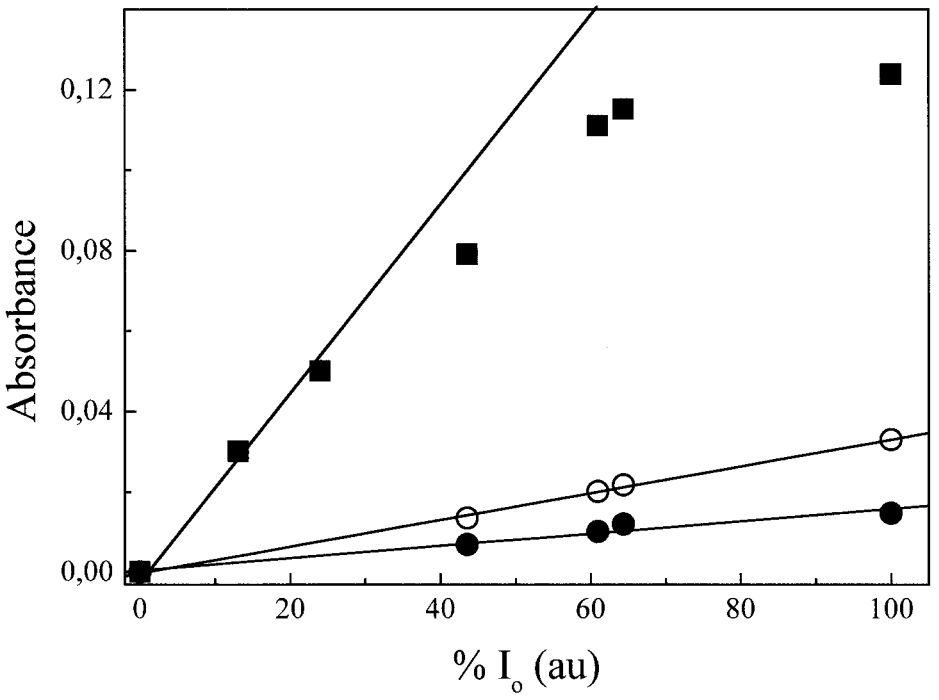


Figure 5. Absorbance of (●) the 1-naphthylmethyl free radical measured at 330 nm ($A^{R\cdot}_{330}$), (○) the triplet–triplet absorption of salt **I** measured a 420 nm, and (■) the triplet–triplet absorption of naphthalene in cyclohexane measured at 413 nm as a function of the laser intensity.

triplet absorption of the salt (taken to be identical to that reported for triplet–triplet absorption of MN, i.e., 14, 200 M − 1 cm^{-1}).[21] The other variables in eq 2 were already defined. Accordingly, the experimental value of Φ^{I}_{isc} is 0.17 ± 0.04.

Taking advantage of the relatively long lifetime observed for the triplet state of the salt, we carried out a series of experiments in which the triplet state was selectively quenched. The main goal of these experiments was to obtain information concerning the nature of the excited-state precursors in the formation of the 1-naphthylmethyl radical. The quencher used was piperylene, which is particularly appropriate for this study because it does not show significant absorption at 266 nm. It is also worth noting that at the concentrations of the diene used in these experiments (<2.0 10^{-3} M), the singlet excited state of the salt is not quenched. Because of the poor solubility of piperylene in water, all experiments were performed in acetonitrile.

The triplet lifetimes of **I** was efficiently reduced by the addition of piperylene. An analysis of the experimental data showed that the quenching process followed a typical Stern–Volmer behavior. From the slope and intercept of the linear plot of ($1/\tau^{T}$) versus the piperylene concentration, a bimolecular rate constant (k_q) of 1.5 × 10^9 M^{-1} s^{-1} and a τ_0^T value of 4.5 μs were calculated. Taking into account that the triplet energies of the MN chromophore and piperylene are 2.63[24] and 2.56 eV,[26] respectively, we find that the observed k_q value is in agreement with that expected for a slightly exergonic triplet–triplet energy-transfer process.

Triplet excited-state quenching of **I** by piperylene is accompanied by a decrease in the absorption corresponding to the 1-naphthylmethyl free radical. The reduced efficiency for the formation of the radical in the presence of the quencher may be explained with the mechanism shown in Scheme 2. ^{1,3}**I*** represents the singlet (or triplet) excited state of the salt, and R · and Q stand for the free radical and quencher, respectively. In this mechanism, it is assumed that R · can be formed from both excited states, and the formation of the other products arises only from the singlet excited state. Both suppositions are discussed in the Discussion section.

According to the mechanism, the total quantum yield for the formation of the free radical ($\Phi_{R\cdot}$) is given by

$$\Phi_{R\cdot} = \Phi^{S}_{R\cdot} + \Phi^{T}_{R\cdot} \qquad (3)$$

$$\mathbf{I} \xrightarrow{h\nu} {}^1\mathbf{I}^*$$

$${}^1\mathbf{I}^* \xrightarrow{k_g^S} \mathbf{I}\ (+h\nu_f \text{ or } kT)$$

$${}^1\mathbf{I}^* \xrightarrow{k_{isc}} {}^3\mathbf{I}^*$$

$${}^1\mathbf{I}^* \xrightarrow{k_{R\cdot}^S} R\cdot$$

$${}^1\mathbf{I}^* \xrightarrow{k_p^S} \text{other products}$$

$${}^3\mathbf{I}^* \xrightarrow{k_g^T} \mathbf{I}\ (+h\nu_p \text{ or } kT)$$

$${}^3\mathbf{I}^* \xrightarrow{k_{R\cdot}^T} R\cdot$$

$${}^3\mathbf{I}^* + Q \xrightarrow{k_q} \text{quenching}$$

Scheme 2

where Φ_R^S. and Φ_R^T. are the quantum yields for radical formation from the corresponding excited state. Φ_R^T. can be written as follows:

$$\Phi_{R\cdot}^{T} = \frac{\Phi_{isc}^{I}\Theta_{R\cdot}^{T}}{(1 + k_q\tau_o^T[Q])} \tag{4}$$

where $\Theta_{R\cdot}^{T}$ represents the efficiency of the triplet state of the salt for yielding the free radical and Φ_{isc}^I (~0.17 ± 0.04) is the corresponding intersystem crossing quantum yield. Figure 6 shows a plot of Φ_R. versus $1/(1 + K_{SV}[Q])$. The Φ_R. values were calculated from the absorption of the radical measured at 330 nm ($A_{330}^{R\cdot}$) and under the assumption that $\epsilon_{330}^{R\cdot}$ is approximately 20,000 ± 10,000 M^{-1} cm^{-1}. An inspection of Figure 6 shows that the plot is linear, and its intercept is a positive value above the experimental error. According to the aforementioned mechanism, this result indicates that both states contribute to the formation of R · . The slope and intercept of the plot in Figure 6 are 0.010 ± 0.005 and 0.043 ± 0.002, respectively. These values were used to calculate Φ_R^S. and Θ_R^T. (eqs 3 and 4). The values obtained are Φ_R^S. = 0.010 ± 0.005 and Φ_R^T. = 0.25 ± 0.20. The total quantum yield for the formation of the free radical in acetonitrile (Θ_R. = Φ_R^S. + $\Phi_{isc}^I\Theta_R^T$.) in the absence of a quencher is 0.05 ± 0.02, which is very similar to that obtained in aqueous basic solutions (0.06 ± 0.04).

The reactivity of the triplet excited state of the salt with the vinyl monomers was also investi-

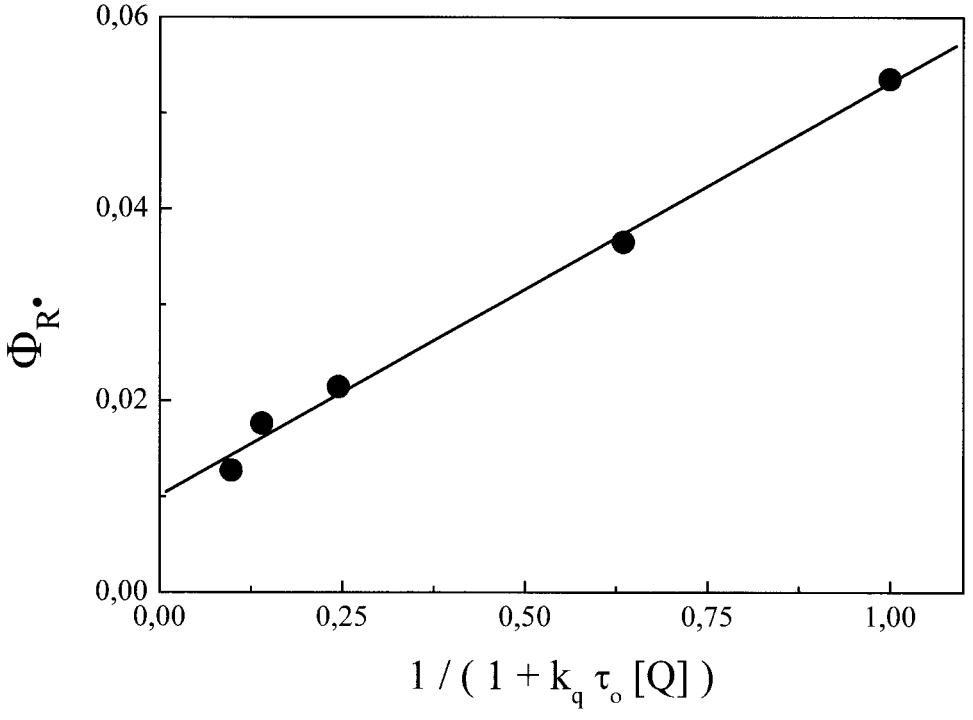
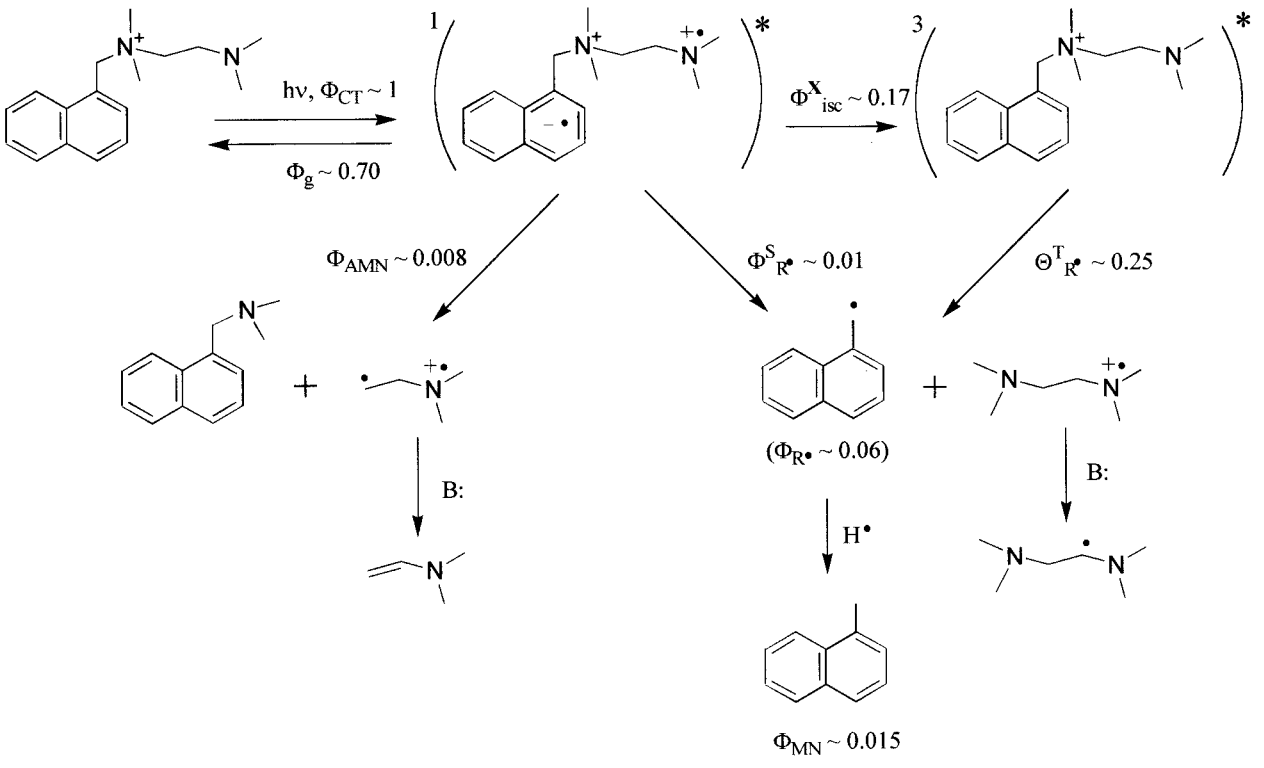


Figure 6. Φ_R. versus the concentration of pyperilene. The slope and intercept are 0.010 ± 0.005 and 0.043 ± 0.002, respectively.



Scheme 3

gated. In basic solutions, the lifetime of the triplet state is not modified by the presence of 0.02 M AA (or HEMA). Unfortunately, both monomers have a significant absorption at 266 nm, which confines this particular study to relatively dilute solutions. In the same experiment, it was observed that the free-radical lifetime (~100 μs) did not change in the presence of the monomers. This indicates that the rate constant for the addition of the free radical to the double bond is less than 10^6 M^{-1} s^{-1}.

Mechanism of the Photodecomposition of I

In Scheme 3 is proposed a mechanism for the photodecomposition of **I** in aqueous solutions that is in agreement with most of the experimental results. According to this mechanism, after excitation of the naphthalene chromophore, **I** undergoes a fast intramolecular ET reaction to form the radical ion pair (RIP). The Gibbs energy change (ΔG) associated with the formation of the RIP can be calculated by the Weller equation:[27] $\Delta G \cong e(E^D_{ox} - E^A_{red}) + w - E_{0-0}$, where E^D_{ox} and E^A_{red} represent the oxidation potential of the electron donor and the reduction potential of the electron acceptor, respectively; E_{0-0} is the energy of the excited chromophore; and w is the free energy gained by the formed ions being brought from infinity to a given encounter distance. In polar solvents, a value of -0.06 eV for w is generally accepted.[28] Therefore, with the oxidation and reduction potentials of **I** measured in acetonitrile (i.e., +0.98 V and −2.03 V vs SCE, respectively) and the singlet (3.91 eV) and triplet (2.64 eV) excited-state energies of the MN chromophore,[29] ΔG values of −0.96 eV and +0.31 eV for the singlet and triplet ET processes are calculated. These values clearly suggest that the intramolecular ET reaction from the singlet excited state should be spontaneous, whereas an ET reaction should not be expected from the triplet excited state of the naphthalene chromophore. The fast formation of the singlet RIP competes favorably with the emission of an aromatic chromophore, explaining the poor fluorescence (and short emission decay time) of **I** in basic and aprotic media. At this point, it seems reasonable to assume that the formation of the RIP occurs with near unity efficiency ($\Phi_{CT} \cong 1$).

The singlet RIP decays through the following nonradiative pathways:

1. Back ET to the ground state. This should be the main decay route of the RIP intermediate. An approximated quantum yield value for this process ($\Phi_g \cong 0.70$) can be calculated

taking into account the efficiency of the other competitive pathways.

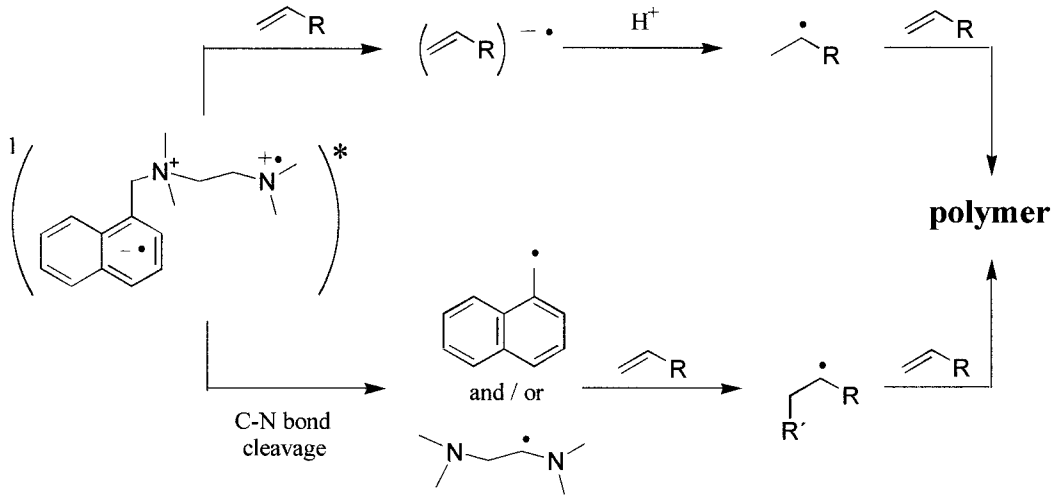
2. Decomposition of the RIP intermediate. Thermal decomposition of the RIP is postulated to explain the formation of AMN and MN generated from the singlet excited state of the salt. Accordingly, we propose an intramolecular $\pi^* \rightarrow \sigma^*$ ET reaction occurring from the aromatic anion radical to the C—N bonds centered on the ammonium nitrogen of the salt; therefore, C—N bond cleavage in the RIP intermediate may produce either AMN ($\phi_{AMN} = 0.008$) or the 1-methylnaphthyl free radical ($\Phi_R^S . = 0.01$), depending on the nature of the σ^* acceptor orbital. In principle, this process could be considered a concerted ET/bond-cleavage reaction similar to that occurring in the one-electron reductive fragmentation of C—Cl bonds.[30] Note that during the C—N bond cleavage, to form the 1-methylnaphthyl free radical also, an amine cation radical is produced. In basic media, it is known that amine cation radicals deprotonate quickly to give the corresponding amine radical.[31,32] The amine cation radical produced from the decomposition of the RIP state to yield AMN is expected to follow a similar process to give a (hydrolyzable) vinylamine.
3. Back ET (with spin inversion) to yield the triplet excited state of the salt. Because the RIP is formed with near unity efficiency, population of the triplet state of the salt must occur from the charge-transfer state intermediate. Therefore, the intersystem crossing ($\Phi_{isc}^I \cong 0.17$) process should involve a back ET reaction coupled with spin inversion. This is a usually observed pathway decay of RIP states due to electron-donor (D) or electron-acceptor (A) local triplet excited states laying the RIP energy.[33,34] According to the calculations with the Weller equation, in the particular case of **I**, this process should be thermodynamically favorable by about 0.31 eV. The triplet may also decompose to the 1-methylnaphthyl free radical and the corresponding amine cation radical through homolytic C—N bond scission. This is feasible process, as established by Pincock et al.,[20] for the photodecomposition of several tetraalkylammonium salts in methanol. As shown in the triplet quenching experiments, the decomposition of the salt from this state is the principal source of 1-naphthylmethyl free radical. Note that AMN is not formed from the triplet of the salt. Although this product could also arise from triplet RIP, the formation of the charge-transfer state in this particular spin multiplicity is thermodynamically unfavorable.

Polymerization Initiation Mechanism

As shown in the fluorescence and flash photolysis experiments, the vinyl monomers do not interact with the singlet and triplet excited states of **I**. Therefore, the polymerization initiation step necessarily must involve the reaction of the monomers with one (or more) of the reaction intermediates formed during the photodecomposition of the salt. According to the mechanism proposed, the amine and 1-naphthylmethyl free radicals and the RIP state are able to act as potential initiators of a vinyl polymerization. Scheme 4 shows possible reaction routes between these radicals intermediate and the vinyl monomers.

Amine cation radicals and their corresponding amine radicals were suggested as initiators of the vinyl polymerization.[35–38] However, according to the experimental results of Iwai and coworkers[4,12] the radicals arising from triethylamine do not initiate the polymerization of AA in a water solution. On the other hand, as for alkyl, phenyl-, benzyl-, and benzoyl-free radicals, the 1-naphthylmethyl radical formed upon the photolysis of **I** should also be able to initiate vinyl polymerization. Although the upper limit rate constant measured in the flash photolysis experiments for the addition of this radical to the vinyl substrates is only 10^6 M^{-1} s^{-1} or less, this process cannot be disregarded because the polymerization of acrylate monomers can be triggered by some free radicals with rates constants lower than 10^4 M^{-1} s^{-1}.[39,40]

Another possibility of initiation involves an ET reaction between the RIP intermediate and the monomer, as suggested in Scheme 4. This reaction should be a spontaneous process considering that the reduction potential of the vinyl monomers in acetonitrile is in the range of -1.2 to -2.0 V (vs SCE)[4,7] and the oxidation potential of the RIP can be taken as that of the naphthalene radical anion, that is, $+2.03$ V.[41] Under such considerations, the ΔG value for the ET process must be around 0 to -0.8 eV. Unfortunately, the RIP emission is not observed in the solvents studied; otherwise, the bimolecular rate constant for the interaction between the RIP and the monomer could be calculated experimentally. However, on the basis of the calculated ΔG values, the rate constants for the process



Scheme 4

should be near the diffusional regime ($\geq 10^9$ M^{-1} s^{-1} in water). Therefore, assuming a RIP lifetime of approximately 1 ns (which is a small value compared with those reported for the lifetime of analogous RIP in polar solvents[33]), the fraction of interception of the RIP by the monomer at a concentration 1 M is approximately 0.5. It is concluded that the ET process probably represents the main decay pathway of the RIP under the polymerization conditions studied. After formation, the anion radical of the vinyl substrate protonates and initiates the chain reaction.

CONCLUSIONS

Salt **I** was found to be an effective initiator of the vinyl polymerization of AA and HEMA in water and organic media and styrene in dichloromethane.

Upon irradiation at 320 nm and in the absence of monomers, **I** undergoes a fast intramolecular ET reaction to form a singlet excited RIP state. This ionic intermediate decomposes to yield AMN and MN. The RIP state also yields the triplet excited state of **I**, which undergoes C—N homolytic bond cleavage to form MN. From flash photolysis experiments, it has been shown that both the singlet and triplet excited states of the salt contribute to the formation of MN.

In the course of the photodecomposition of the salt, several species able to act as initiators of a vinyl polymerization are formed. According to the mechanism proposed, these species are the singlet excited-state RIP, amine radicals, and the 1-naphthylmethyl free radicals. Salt **I** was tested for its usefulness for photoinitiating vinyl polymerization even when used at concentrations of about 1.0×10^{-5} M. This is related to the capacity of **I** to generate active species by a unimolecular process. Although the ammonium group in **I** was included for the purpose of increasing its solubility in water, it has been demonstrated that it has an important role in the photodecomposition of the salt. The vinyl substrates may interact with one or all the radical species present, depending on the concentration of the monomer employed. At a 1 M monomer concentration, the most probable initiation mechanism involves an ET reaction between the RIP state and the vinyl substrate. In such a reaction, the vinyl anion radical should be formed. Subsequent protonation of the radical anion provides the corresponding neutral species, which starts the polymerization chain reaction. At low concentrations of the monomers, the interception of the RIP intermediate is quite improbable; therefore, the initiation mechanism should involve the reaction of the vinyl substrates with amine radicals and the 1-naphthylmethyl free radicals arising from the photodecomposition of **I**.

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